The role of carboxylic acids on a Na_2WO_4/H_2WO_4-based biphasic homogeneous alkene epoxidation, using H_2O_2 as oxidant

Palanisamy Uma Maheswari [a], Xiaohua Tang [a], Ronald Hage [b],
Patrick Gamez [a], Jan Reedijk [a,*]

[a] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*
[b] *Unilever R&D Vlaardingen, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands*

Abstract

The role of various carboxylic acids (substituted/unsubstituted acetic, benzoic and salicylic acids) with various electron donating and/or withdrawing substituents on the Na_2WO_4/H_2WO_4-catalysed, biphasic epoxidations of cyclooctene and 1-octene, using H_2O_2 as terminal oxidant has been investigated. The presence of the different acids in catalytic amounts widely affects the catalytic activity of the above system depending on the nature of their substituents. The results obtained have been discussed in the light of the stereo/electronic effects of these substituents. It has been observed that the added substituted/unsubstituted acetic and benzoic acids generally enhance the rate of the epoxidation while salicylic acids significantly decrease the catalyst activity, under the same conditions, most likely due to the additional deactivating hydroxy moiety.
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1. Introduction

In the development of efficient and environmentally benign oxidation processes, hydrogen peroxide holds a prominent place among the other oxidants. The advantages of H_2O_2 are its low cost, high active oxygen content, high oxidation potential, and the formation of only water as a reduction product [1,2]. However, the main drawback is the high activation energy required for the oxidation of many organic compounds by H_2O_2. Therefore, catalysts are often required to perform efficient H_2O_2-mediated oxidation reactions. Over the years, a number of catalysts based on transition metal ions like Ti, W, Mo, Fe, Mn and Re have been reported for the *in situ* activation of H_2O_2 for the epoxidation of olefins [3–8]. Among these, the procedures based on tungsten catalysts are particularly attractive since tungsten is a readily available and inexpensive transition metal, with good catalytic stability and recycling efficiency without any specially designed organic ligands [9–12]. In addition, tungsten is poorly

active towards the unproductive decomposition of H_2O_2, which enhances the atom-efficiency of H_2O_2 [13,14]. A number of tungsten-containing polyoxometalates have been reported as highly efficient catalysts for the epoxidation of alkenes in the presence of an oxygen source like hydrogen peroxide or organic hydroperoxides [15–19].

Among the tungsten systems reported so far, the most active ones are attributed to their residual acidity due to the presence of organic or inorganic acid additives in the catalytic mixtures [11]. The importance of the acidic nature of the tungsten-catalyst precursor species in the *in situ* experiments is illustrated by the fact that the *in situ* Venturello- and Prandi-catalysed cyclooctene epoxidation show negligible activities when H_2WO_4 is replaced by Na_2WO_4, which generates sodium hydroxide as the result of the formation of peroxotungstate species with H_2O_2 [20]. In this respect, it is remarkable that the Noyori system, which is also based on Na_2WO_4, does show appreciable activities, most likely owing to the acidic HSO_4^- anion in the phase transfer catalyst [21]. In line with the strong activity increase with H_2WO_4 instead of Na_2WO_4 as the tungstate source in the Venturello and Prandi systems, the performance of the Noyori system is significantly improved when H_2WO_4 is used in place of Na_2WO_4 [22].

However, H_2WO_4 is poorly soluble in H_2O and H_2O_2 and the systems require higher temperatures ranging from 60 to 90 °C for activation. In this regard, self-assembling catalysts like Sandwich polyoxometalate NaZnPOM and Luviquat mono CP is very much appreciable, as a multifunctional co-catalyst with the established emulsifying, buffering and phase-transferring properties for various oxidative transformations with H_2O_2, such as epoxidation, heteroatom oxidation, and alcohol oxidation and also can be prepared *in situ*, with these multifaceted properties [16,23,24].

In order to decrease the reaction temperature without lessening the oxidation rate, or even enhancing it, some additives can be used to tune catalytic activity. The possible additives range from strong acids and bases to mild acids and bases including some buffering systems [25]. The typical epoxidation reagents are mainly organic peroxides or peracids which are industrially dangerous to handle and to store. However, the important benefit in using such organic reagents is that their stereo-electronic nature can easily be modified by changing their substituents appropriately, allowing efficient stereo-selective applications [26–28]. Recently, it was shown that perfluorinated alcoholic solvents such as 2,2,2-trifluoroethanol and particularly 1,1,1,3,3,3-hexafluoro-2-propanol are able to activate H_2O_2 for the epoxidation of electron-rich alkenes without the presence of any metals [29–31]. When polyfluorinated quarternary ammonium salts are used as counter-ions of polyoxometalates, the resulting catalysts are highly effective for oxidation reactions under biphasic conditions in fluorous as well as in common solvents [32].

It has also been reported that several substituted phenols are able to activate hydrogen peroxide effectively through hydrogen bonding resulting in significant rate enhancements without any metal catalysts [33].

Lately, we have introduced a tungsten-based catalytic system, consisting of equivalent amounts of Na_2WO_4 and H_2WO_4, catalytic amounts of monochloroacetic acid and Aliquat 336, which appears to be highly efficient for the biphasic epoxidation of alkenes [34]. The use of a 1:1 Na_2WO_4/H_2WO_4 mixture increases the solubility of H_2WO_4 in H_2O_2 at ambient temperatures. In the present study, different substituted/unsubstituted acetic, benzoic and salicylic acids have been used as additives to appraise the influence of the stereo-electronic properties of the various substituents (Scheme 1). The investigations have been restricted to two alkenes, i.e. cyclooctene and 1-octene, since cyclooctene is easily epoxidized and forms a stable epoxide and 1-octene is a challenging substrate due to its relatively poor reactivity.
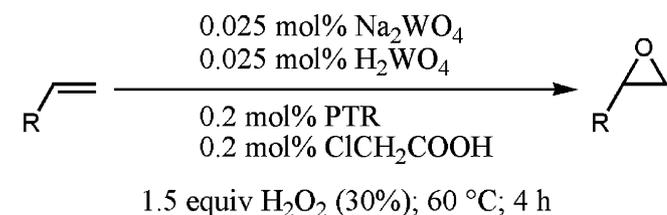
Scheme 1. Epoxidation of alkenes with the catalyst system.

2. Experimental

2.1. Materials

Sodium tungstate and tungstic acid were reagent grade and used as such. All the substituted/unsubstituted carboxylic acids were purchased from Sigma–Aldrich and used as received. The aqueous H_2O_2 solution (30 wt.%) was stored at 4 °C. Gas chromatography (GC) measurements were performed on a HP 6890 Series equipped with a CPSil 5 column (25 m × 0.25 mm; film thickness: 1.20 μm).

2.2. Epoxidation procedure

The oxidations were carried out in air in a 100 mL three-necked round-bottomed flask equipped with a magnetic stirrer and reflux condenser. Typically, 0.033 g (0.1 mmol) of $Na_2WO_4 \cdot 2H_2O$ and 0.025 g (0.1 mmol) of H_2WO_4 were stirred for 2 min in 1 mL of distilled water and then 1.5 equiv. per alkene (75 mmol) of H_2O_2 (30%) were added followed by 0.8 mmol of the carboxylic acid at 60 °C. This mixture was stirred for 5 more minutes followed by the addition of 50 mmol of the alkene and 0.2 mmol of methyltri-*n*-octylammonium chloride (Aliquat 336, phase transfer reagent). The oxidation reaction was started without any incubation period. Samples were collected from the organic phase regularly to monitor the oxidation by GC (1,4-dibromobenzene; 1 mg mL^{-1} in CH_2Cl_2; GC internal standard) for analyses. The products of the reaction were determined by comparison with the commercially available compounds. Thus, in all the epoxidation reactions carried out, the byproducts represented less than 1% conversion and were identified as cyclooctane diol and suberic acid.

3. Results and discussion

3.1. Influence of acetic acids on the epoxidation of cyclooctene catalysed by the Na_2WO_4/H_2WO_4 system

The presence of various acetic acids, in catalytic amounts, affects the rate of conversion of cyclooctene to cyclooctene oxide depending on the substituents as shown in Figs. 1 and 2. Thus, the cyclooctene oxide formation is observed within a range of 62–99%, after a reaction time of 4 h. The effect of one or more halogen substituents on the acid is dramatic. Indeed, the monochloroacetic acid gives the highest conversion, i.e. 99% (92% conversion is reached after 1 h reaction time) while the unsubstituted acetic acid give 94% cyclooctene oxide in 4 h (and only 70% conversion is observed after 1 h). The exchange of the chloride atom to a bromide results in a decrease of the catalytic activity, reflecting the ambivalent character of halides. Indeed, halogen substituents principally act as electron withdrawing groups due to their electronegativity but they are also electron donating groups as a result of the presence of electron lone-pairs. Thus, the donating character of the bromide is apparently higher than for the chloride, which leads to a lower conversion. Accordingly, the presence of a second or a third chloride atom gives rise to a significant decrease of the catalyst efficiency, suggesting a
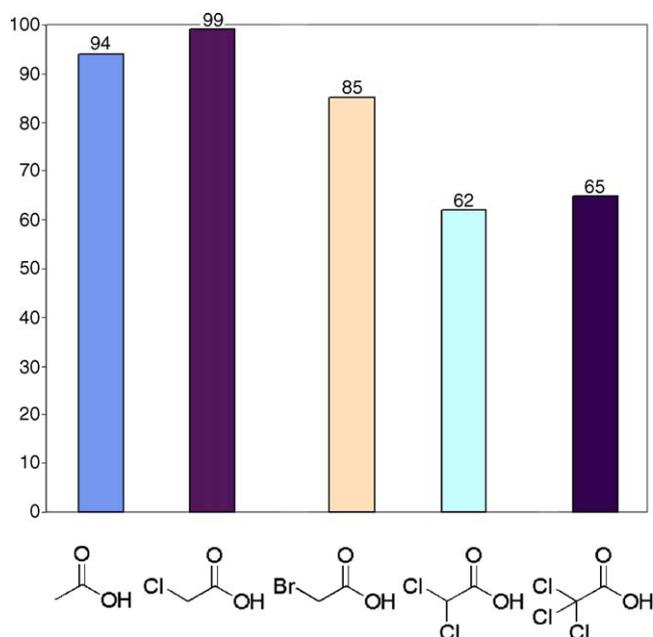
Fig. 1. Plot of % conversion to cyclooctene oxide obtained using halogenated acetic acid derivatives, after 4 h reaction time, in the presence of Na$_2$WO$_4$/H$_2$WO$_4$/Aliquat 336/H$_2$O$_2$ at 60 °C.

Fig. 2. Plot % conversion to cyclooctene oxide obtained using various substituted acetic acid derivatives, after 4 h reaction time, in the presence of Na$_2$WO$_4$/H$_2$WO$_4$/Aliquat 336/H$_2$O$_2$ at 60 °C.

greater involvement of the combined donating effects of several halides. This result is confirmed with the use of aminoacetic acid as additive, since the lowest conversion is observed (Fig. 2) in the presence of a strong donating group (Fig. 3). The acetic acid derivatives holding substituents which provide inductive
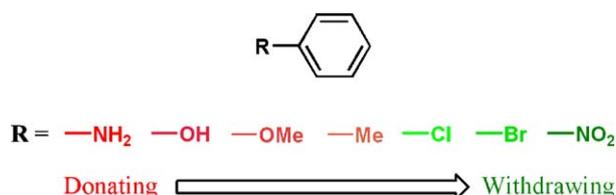

Fig. 3. Donating and withdrawing substituents.

and/or resonance effects do not notably affect the conversion rates, e.g. trimethylacetic acid (90% conversion), phenyl and diphenylacetic acid (92 and 90% conversion, respectively).

In addition, the conversions achieved for the oxidation of cyclooctene using acetic acids with different electron donating substituents, much weaker than the amino group (Fig. 3), namely the methoxy and n-butyl groups, are comparable to the one obtained with bromoacetic acid (Fig. 1). This observation clearly indicates that only strong donor groups significantly influence the reaction rates, which is noted as well for the benzoic acid derivatives. Finally, thioacetic acid gives a conversion of 91% in 4 h reaction time, revealing the absence of effect induced by the sulfur atom.

3.2. Influence of benzoic acid derivatives on the epoxidation of cyclooctene catalysed by the Na$_2$WO$_4$/H$_2$WO$_4$ system

The use of benzoic acids with electron withdrawing or electron donating substituents leads to conversions ranging from 41 to 93%, as shown in Figs. 4–6. The influence of different halides on the catalytic activity has been examined and the results are reported in Fig. 4. No dramatic effect is noticed and the position (*ortho*, *meta*, or *para*) of the halogen atom on the aromatic ring does not modify at all the catalyst efficiency. In contrast to the halogenoacetic acid derivatives, the nature of the halide does not alter the catalytic performance since the use of 4-chloro-, 4-bromo-acid, or 4-iodobenzoic acid leads to comparable conversions of 91, 91 and 87%, respectively. In the case of benzoic acid additives, the withdrawing/donating effects of the halide substituents are less important, most likely owing to a 'dilution' of the electronic influence due to a delocalization with the aromatic ring.
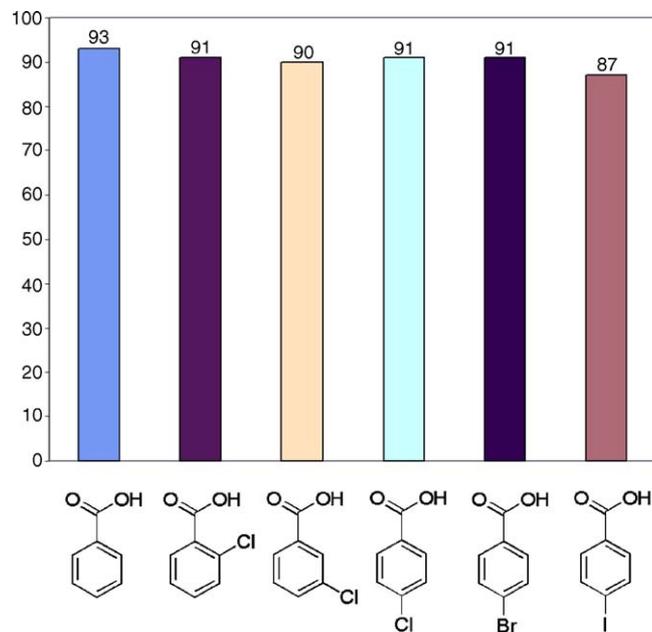

Fig. 4. Plot of % conversion to cyclooctene oxide obtained using various halogenated benzoic acid derivatives, after 4 h reaction time, in the presence of Na$_2$WO$_4$/H$_2$WO$_4$/Aliquat 336/H$_2$O$_2$ at 60 °C.
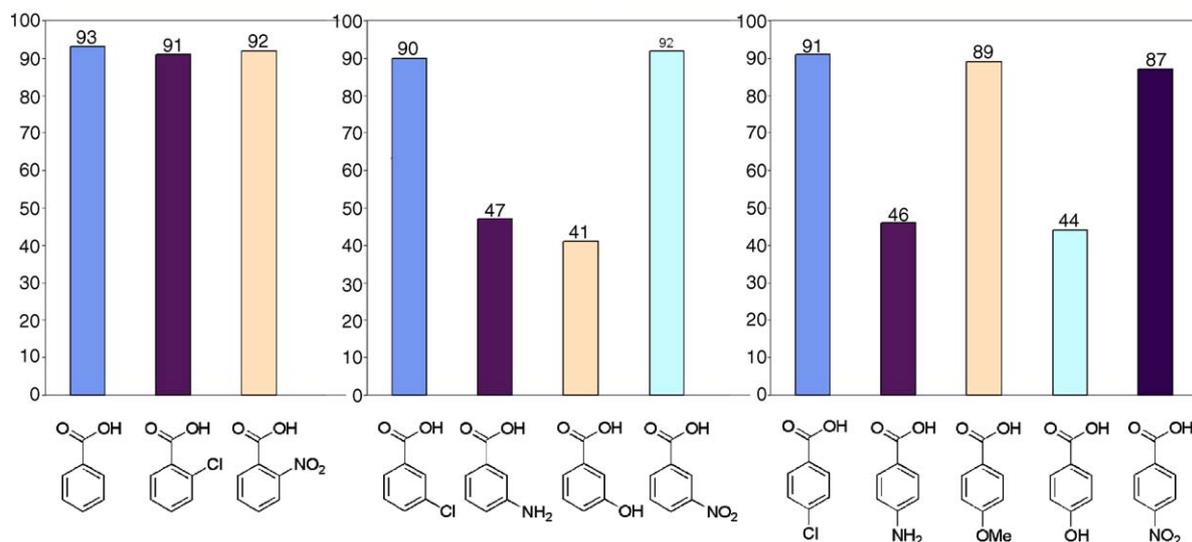
Fig. 5. Plot of % conversion to cyclooctene oxide obtained using various *ortho*-, *meta*-, or *para*-substituted benzoic acid derivatives, after 4 h reaction time, in the presence of Na_2WO_4/H_2WO_4/Aliquat 336/H_2O_2 at 60 °C.

Next, a series of *ortho*-, *meta*-, and *para*-substituted benzoic acids have been tested as additives and the results are depicted in Fig. 5. Strong donor groups like amine or hydroxy dramatically reduce the efficacy of the resulting catalytic mixture. On the contrary, the strong electron withdrawing nitro group does not modify at all the catalytic activity independently of its position on the aromatic ring, showing once again the sole influence of donating groups on the catalyst efficiency. Indeed, 3- and 4-amino benzoic acids lead only to 47 and 46% conversion to

Fig. 6. Plot of % conversion to cyclooctene oxide obtained using different benzoic acid derivatives, after 4 h reaction time, in the presence of Na_2WO_4/H_2WO_4/Aliquat 336/H_2O_2 at 60 °C.

cyclooctene oxide, respectively. The same effect is observed with 3- and 4-hydroxybenzoic acids which merely give 41 and 44% yield in cyclooctene oxide, respectively, in 4 h reaction time. These conversions to cyclooctene oxide are significantly inferior to the one achieved in the absence of any carboxylic acid (60% conversion to cyclooctene oxide within 4 h reaction time), demonstrating the detrimental influence of an electron donating substituent on the additive. Similarly to the acetic acid additives, the weaker electron donating methoxy group does not instigate any catalyst alteration since a conversion of 89% is reached.

Finally, the influence of more than one substituent on the aromatic ring as well as the presence of a sulfur atom is reported in Fig. 6. The use of thiobenzoic acid gives a conversion of 88%. The combination of three weak electron donating methyl groups (Fig. 3), when using 2,4,6-trimethylbenzoic acid, results in, as expected regarding the observations described above, a notable decrease in activity from 93% for benzoic acid to 80% for the trialkyl substituted additive. This synergistic donating effect is further confirmed with 3-methoxy-4-hydroxy-benzoic acid where the addition of the weak methoxy substituent to 4-hydroxy-benzoic acid gives rise to a 9% decrease of the conversion, after a reaction time of 4 h.

3.3. Influence of salicylic acid derivatives on the epoxidation of cyclooctene catalysed by the Na_2WO_4/H_2WO_4 system

Compared to the unsubstituted/substituted acetic acids and benzoic acids, the salicylic acid derivatives relatively give inferior conversions to cyclooctene oxide as shown in Figs. 7–9.

These general lower catalytic activities are obviously due to the *ortho*-hydroxy group of the salicylic acid derivatives which highly inhibits the oxidation reaction rate. One possible explanation is the binding of the salicylic acid derivative to the tungsten atom in a bidentate fashion, through both the carboxylic and
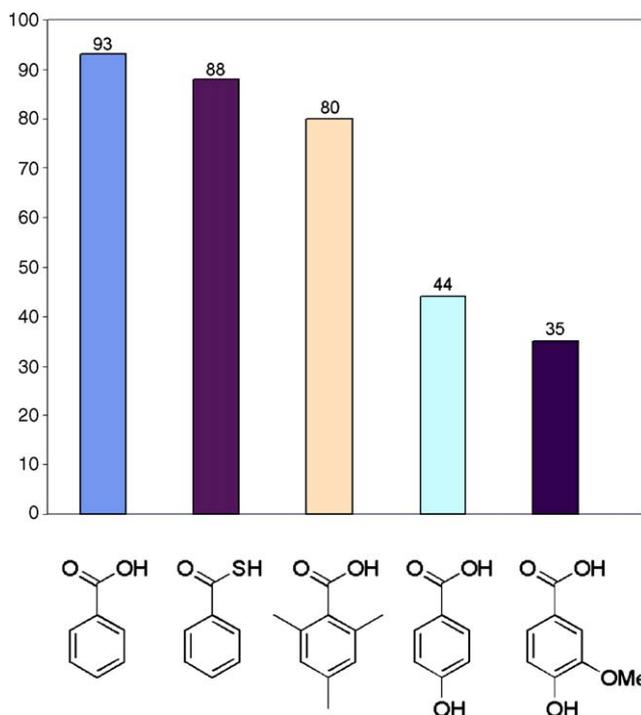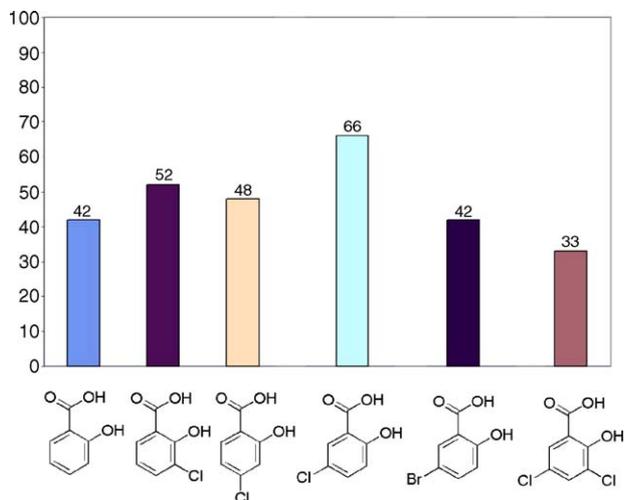
Fig. 7. Plot of % conversion to cyclooctene oxide obtained using halogenated salicylic acid derivatives, after 4 h reaction time, in the presence of Na_2WO_4/H_2WO_4/Aliquat 336/H_2O_2 at 60 °C.

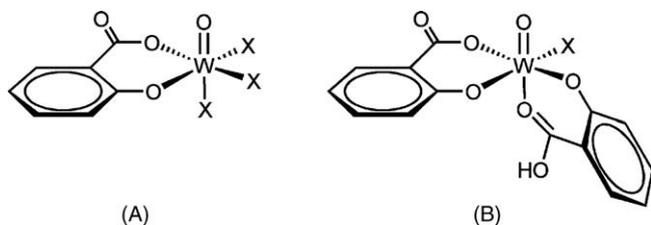
Fig. 8. Schematic representations of [W(salicylic acid)] complexes reported in refs. [35,36].

the hydroxy groups (Fig. 8). This type of coordination has previously reported in refs. [35,36], and may justify the lower efficiency of the resulting catalysts due to a decrease of the coordination sites on the metal centre (structures A and B, Fig. 8).

However, salicylic acid gives a conversion of 42% to cyclooctene oxide, analogous to the one achieved with 4-hydroxy benzoic acid (44%, Fig. 6), which leans towards the influence of the donating/withdrawing effects on the catalytic activity rather than a bidentate coordination of the additive. The presence of a chloride atom in the aromatic ring at the *ortho-*, *meta-*, or *para*-position relative to the OH group, gives rise to interesting results, reflecting the resonance effect of this hydroxy substituent (Fig. 9). Indeed, the chloride atom at the *ortho-* or at the *para*-position leads to significant improvement of the catalyst efficacy. The electron donating effect due to the hydroxy group is minimized since the inductive character of the chloride atoms compensates the negative charges located at the *ortho-*
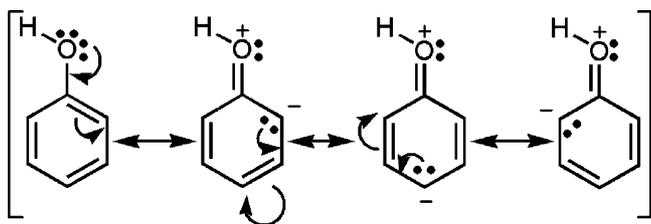

Fig. 9. Resonance effect in the phenol ring.

and *para*-carbon atoms of the aromatic ring (Fig. 9). Therefore, higher catalytic activities, compared to the one obtained with the halogen-free salicylic acid, are observed and this effect is not surprisingly more pronounced with the *para*-chloride substituent (Fig. 7). As expected, the influence of the *meta*-chloride atom is lesser, and only a small increase of the conversion is observed (48% instead of 42% for salicylic acid). In haloarenes, both inductive and resonance contributions play an important role which is suggested by the use of 4-bromo salicylic acid (Fig. 7). The bromide atom has no influence on the catalytic activity in contrast to the 4-chloro derivative. This variation between the chloride and the bromide groups has been also observed in the case of acetic acids (Fig. 1).

The very low conversion achieved with 3,5-dichlorosalicylic acid is, a priori, not easily explainable. One would expect that the combination of the *ortho-* and the *para*-chloride atoms would generate the best system, which is obviously not the case. In fact, this acidic additive combines many electron donating (hydoxy and chloride groups) and withdrawing (carboxylic and chloride groups) effects. It has been shown with the acetic acids that the presence of more than one chloride atom leads to a catalyst inhibition, justified by a higher contribution of the electron donation owing to the halides (Fig. 1). This consequence is apparently obtained again with this dichlorosalicylic acid (Fig. 7).

Finally, the influence of various electron donating and withdrawing groups on the catalytic activity has been considered with salicylic acid derivatives and the results are reported in Fig. 10. The conversion achieved with the *para*-methoxy (relative to the OH group) derivative corroborates the assumption put forward when examining the result obtained with the *para*-chlorosalicylic acid (5-chlorosalicylic acid, Fig. 7). Indeed,
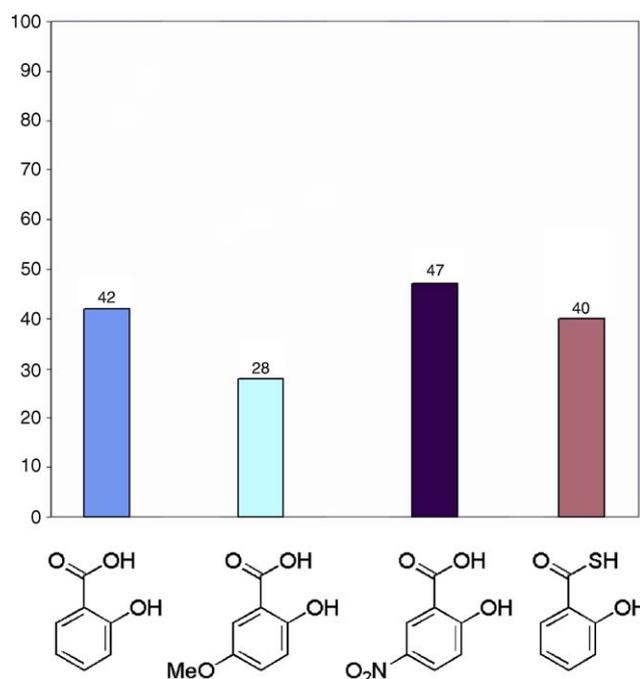

Fig. 10. Plot of % conversion to cyclooctene oxide obtained using different salicylic acid derivatives, after 4 h reaction time, in the presence of Na_2WO_4/H_2WO_4/Aliquat 336/H_2O_2 at 60 °C.

contrary to the chloro substituent, the methoxy group is electron donating; therefore, it does not annihilate the inhibiting character of the hydroxy substituent. In fact, the two effects are apparently merged, which result in the worse catalytic system, with a conversion of only 28% after a reaction time of 4 h. The strong withdrawing nitro group slightly increases the conversion to cyclooctene oxide, as observed for the two other types of carboxylic acids. Lastly, the use of thiosalicylic acid confirms the non-influence of the sulfur atom on the reactivity of the catalyst.

3.4. Reactivity toward 1-octene

The epoxidation of terminal alkenes is much more difficult to achieve [37,38]. In the present study, the epoxidation of 1-octene in the presence of all the carboxylic acids mentioned above generally results in very low conversions to the epoxide (2–8%). Exceptionally, the use of monochloroacetic acid or trimethylacetic acid as additives yields 28 and 35% of 1-octene oxide, respectively, after a reaction time of 8 h. These conversions correspond to turnover numbers of respectively, 70 and 87, which are very good for aliphatic terminal olefins.

3.5. General discussion

In line with the activation of hydrogen peroxide by transition metal complexes, a major breakthrough is the observation of oxodiperoxo neutral or anionic tungsten(VI) and molybdenum(VI) species, starting from the simple sodium salts or tungstic or molybdic acids in the presence of aqueous hydrogen peroxide at ambient temperature conditions [39]. The addition of phosphate, arsenate or sulfate to the above oxodiperoxo species results in high nuclearity clusters, usually denoted as PW2, PW4 and so on. Many polyoxometalate species such as the Keggin dodecatungstophosphate anion of $H_3[PW_{12}O_{40}]_{aq}$ are effective systems for numerous oxidation procedures in the presence of H_2O_2 [40]. However, all the high nuclearity species, including the polyoxometalates, are considered to be the 'catalyst precursors' for the formation of the 'actual catalysts', i.e. mono/dinuclear oxoperoxo-tungsten species, for the epoxidation toward alkenes, which depends on several parameters like concentration of H_2O_2, solvent, temperature, or pH of the aqueous phase in case of the biphasic catalysis. The peroxo bridged high-nuclearity tungsten species are convincingly proved to be less active toward oxygen atom transfer than the lower nuclearity species [41]. Thus, a high incubation period, at high temperatures, in the presence of (60–80%) H_2O_2 and an aqueous acidic medium are often required for oxidation procedures involving polyoxometalates. Most importantly, the acidic nature of the medium seems to enhance the oxygen atom transfer efficiently, as observed, remarkably for the Noyori system, even though the real cause of this effect, is yet to be elucidated. The phosphate coordination to tungsten in PW2 and PW4 is thought to increase the electrophilic character, of the η-coordinated peroxo species, thus facilitating the oxygen atom transfer to the alkene [42].

In earlier work on [Na_2WO_4/H_2WO_4]-catalysed epoxidations [34], we have observed from ESI-MS experiments, that mono/dinuclear oxo-peroxo with coordinated chloroacetic acid

rather than any high-nuclearity tungsten species act as active catalytic species for the epoxidation of alkenes, in the presence of hydrogen peroxide at ambient temperatures. The effective rate enhancement compared to the acid-free system is most likely due to the relatively increased electrophilicity of the η-coordinated peroxo moiety as a result of the coordination of the chloroacetic acid to the tungsten oxo-peroxo species.

In the present paper, the screening of different substituted carboxylic acids with the aforementioned catalytic system further evidences the electronic influence of the carboxylic acids on the catalytic activity. Thus, electron-withdrawing substituents like the halogen or nitro groups enhance the electrophilic nature of the peroxo moiety and hence give positive rate enhancement, relatively to the unsubstituted acids. Strong inhibiting effects have been observed with electron donating substituents, namely the amino and hydroxy groups. In fact, the rate retarding effect induced by electron-donating groups is more prominent than the rate enhancement caused by electron withdrawing groups. Most likely, an overall strong electron donating character of the carboxylic acid additive leads to the formation of different species, which are obviously not as active as the ones obtained with chloroacetic acid [34]. This lower catalyst efficiency may be due to a stronger coordination of the acid to the metal ion. Moreover, since the carboxylic acid is in a four-fold excess, compared to tungsten atom, the coordination of more than one carboxylate group to the tungsten center may prevent the formation of the dinuclear species which appeared to be present and crucial in the highly efficient chloroacetic acid-containing system previously reported [34]. In addition, the involvement of peracid as oxidant can not be excluded, even though it has been evidenced from ESI-MS measurements that the carboxylic acids do coordinate to the tungsten atom [34]. In principle, the formation of the peracid species is less favored with electron donating groups on the initial carboxylic acid, which can also justify the lower conversions achieved with amino- and hydroxy-substituted acidic additives, and more generally with electron-rich carboxylate ligands.

3.6. Concluding remarks

An efficient tungsten-based catalyst has been developed for the biphasic epoxidation of cyclooctene and 1-octene. Mechanistic investigations on the influence of the carboxylic acid additive have been carried out and its important role in the epoxidation reaction has been clearly confirmed [34]. The following statements can now be drawn.

1. The screening of different substituted carboxylic acids with the Na_2WO_4/H_2WO_4 catalytic mixture shows that the acidic additives do influence the catalyst system widely depending on the electronic nature of their substituents.
2. Electron withdrawing groups on the carboxylic acids slightly enhance the oxidation rate, whereas electron donating groups strongly reduce the activity of the resulting catalytic system.
3. In general, the activation of the catalyst is observed in the following order as: acetic acids > benzoic acids ≫ salicylic acids.

Acknowledgements

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